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RATE EQUATION THEORY FOR ISLAND SIZES AND CAPTURE ZONE AREAS IN SUBMONOLAYER DEPOSITION: REALISTIC TREATMENT OF SPATIAL ASPECTS OF NUCLEATION

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ABSTRACT

Extensive information on the distribution of islands formed during submonolayer deposition is provided by the joint probability distribution (JPD) for island sizes, s, and capture zone areas, A. A key ingredient determining the form of the JPD is the impact of each nucleation event on existing capture zone areas. Combining a realistic characterization of such spatial aspects of nucleation with a factorization ansatz for the JPD, we provide a concise rate equation formulation for the variation with island size of both the capture zone area and the island density.

INTRODUCTION

Determination of the analytic form of the size distribution of islands formed via homogeneous nucleation in the early stages of film growth has been a long-standing challenge. Many proposals exist for the variation with size, s, (measured in atoms) of island densities, N_s. These include qualitative speculation in early theories [1], predictions of continuum quasi-hydrodynamic modeling [2], also recent proposals providing convenient analytic forms [3], and identification with the so-called "capture zone" area distribution [4]. However, all of these fail to incorporate basic qualitative features of precise simulation results obtained ~10 years ago [5].

To resolve this discrepancy, one can develop a rate equation formulation for N_s which requires as input the "capture numbers", σ_s, describing the propensity for islands of different sizes, s, to capture diffusing adatoms. The σ_s are traditionally calculated from a self-consistent diffusion equation analysis of the adatom density near islands [1,6]. This analysis of σ_s is based on a mean-field assumption that the typical environment of each island is independent of its size. However, predictions of such a theory for N_s fail to describe correct behavior. The key to obtaining an exact theory for the island size distribution is the recognition of two essential points [7]. *First*, the island size distribution is simply determined by the size-dependence of the average capture number, σ_s, for each island size, s, as quantified by an exact integral formula [7]. *Second*, this dependence of σ_s on s is qualitatively distinct from mean-field predictions [7].

A useful perspective on adatom capture comes from the feature that the capture numbers describing the growth rate of islands correspond to the area of suitably constructed "capture zones" (CZ's) surrounding the islands [8]. This observation did not in itself lead to a correct theory for N_s [4,8]. One also needs to characterize the relationship between CZ areas and island size: larger islands have on average substantially larger CZ's [7]. Thus, in contrast to the above mean-field picture, there is a subtle correlation between the size and separation of islands.

It thus remains to provide a theory for the dependence of σ_s or A_s, versus s. We follow Mulheran and Robbie [9], who developed rate equations for the joint probability distribution (JPD), $N_{s,A}$, for island sizes, s, and capture zone areas, A_s. However, we replace their idealized picture of nucleation as "fragmenting" existing CZ's. Amar *et al.* [10] also utilized simplified JPD equations to recover non-mean-field behavior of the key quantities. However, their even more simplistic treatment of nucleation yielded artificially narrow CZ area distributions for each island size. Earlier, we developed rate equations directly describing the evolution of the A_s [11], and demonstrated the sensitivity to (and need for a realistic treatment of) nucleation [12].

After describing the deposition model and key quantities, we present the rate equations for the JPD. Next, key spatial aspects of nucleation are described and utilized to analyze the (scaled) rate equations. Finally, we discuss new simulation strategies based on our insights.

DEPOSITION MODEL: SCALING AND FACTORIZATION OF THE JPD

We consider *irreversible island formation* during submonolayer deposition at a rate of F per adsorption site (on a square lattice). Deposited adatoms hop to adjacent sites at rate h (per direction), irreversibly nucleate new islands upon meeting and incorporate with existing islands upon aggregation. Atoms landing on-top of an island are incorporated at the island edge. We assume compact island shapes due to efficient restructuring. At very low coverages, $\theta=Ft$, it suffices to consider simpler "point-island" models [5], where islands occupy only a single site, but carry a size label. Using the lattice constant, a, as the unit of length, N_s are measured per adsorption site, and the adatom diffusion coefficient $D=a^2h$ equals the hop rate h per direction.

"Capture zones" (CZ's), mentioned above, follow from the idea that typically atoms deposited nearby an island within its CZ will aggregate with that island. Thus, the CZ area should measure the capture number for that island, and thus its growth rate. Indeed, one can construct CZ's as "diffusion cells" (DC's) based on the solution of an appropriate diffusion equation for deposited atoms, so that this relationship is *exact* [13]. The theory developed in this paper assumes that the CZ's are constructed as DC's, so that their areas exactly describe capture rates. However, construction of "exact" CZ's is non-trivial, and computationally expensive. Thus, to facilitate acquisition of precise statistics for the JPD, etc., for point islands, we will use Voronoi cells (VC's), which are simply based on the distance from the island centers [7,11,12].

As above, $N_{s,A}$ denotes the density of islands with size s, and CZ area A which includes the area of the island. Then, the density, N_s, of islands of size s satisfies $N_s=\Sigma_A N_{s,A}$, and the average island density satisfies $N_{av}=\Sigma_{s>1} N_s$, and $\theta=\Sigma_s sN_s$. The average CZ area for islands of size s satisfies $A_s= \Sigma_A AN_{s,A}/N_s$, where $A_{av}= \Sigma_{s>1} A_sN_s/N_{av}=1/N_{av}$. For large h/F or large average island size $s_{av}=\Sigma_{s>1} sN_s/N_{av}.\approx\theta/N_{av}$, one introduces $x=s/s_{av}\geq 0$ and $\alpha=A/A_{av}\geq 0$, and writes

$$N_{s,A} \approx N_{av} (s_{av} A_{av})^{-1} F(x,\alpha),\ N_s \approx N_{av} (s_{av})^{-1} f(x),\ \text{and}\ A_s \approx A_{av} a(x). \tag{1}$$

Simulations confirm (1) and further reveal that the normalized CZ area distribution for a single island size does not depend on island size [12]. The latter implies the *factorization relation* [12]

$$F(x,\alpha) = G[\alpha-a(x)]f(x), \tag{2}$$

where G gives the shape of the CZ area distribution, with variance $\int d\gamma G(\gamma)\gamma^2=v$. One can adopt a Gaussian form $G(\gamma)=(2\pi)^{-1/2}v^{-1/2}\exp[-\gamma^2/(2v)]$, although simulations reveal some slight skewness.

RATE EQUATIONS FOR THE JPD AND REDUCED QUANTITIES

Evolution of $N_{s,A}$ is impacted by both island nucleation and growth. For *island growth*, we use the feature that the total growth rate satisfies $r_{tot}=FA$. The effect of *island nucleation* is described in part by the probability $P_{s,A}$ that a nucleation event "impacts" the CZ of area A of an island of size s. This means that the CZ of the just-nucleated island overlaps (and thus reduces) the CZ of this existing island of size s. In the event of such overlap, let $A_{subnuc}(s,A)$ denote the average area of the portion or *subset* of the CZ of the just-nucleated island which *overlaps* the existing CZ of area A. We also need the probability $P^{+}_{s,A}$ that nucleation impacts the CZ of an island of size s so as produce a CZ of area A for that island. See Fig.1. Then, $\Sigma_A P_{s,A} = \Sigma_A P^{+}_{s,A} = P_s$ is the probability that nucleation impacts the CZ of some island of size s. Also, $\Sigma_s P_s = M_0$ equals the average number of existing CZ's overlapped by the CZ of a just-nucleated island, where $M_0 \approx 5.5$ for point islands at $\theta=0.1$ML. Finally, we have the basic evolution equations [12]

$$d/dt\, N_{s,A} = - FAN_{s,A} + FAN_{s-1,A} - P_{s,A}\, d/dt\, N_{av} + P^{+}_{s,A}\, d/dt\, N_{av}\,, \qquad (3)$$

for s>2. The four terms are depicted schematically in Fig.1. We now perform a moment analysis of (3) by first applying $\Sigma_A \bullet$. Noting the cancellation of nucleation terms, one obtains for s>2

$$d/dt\, N_s = - FA_sN_s + FA_{s-1}N_{s-1}. \qquad (4)$$

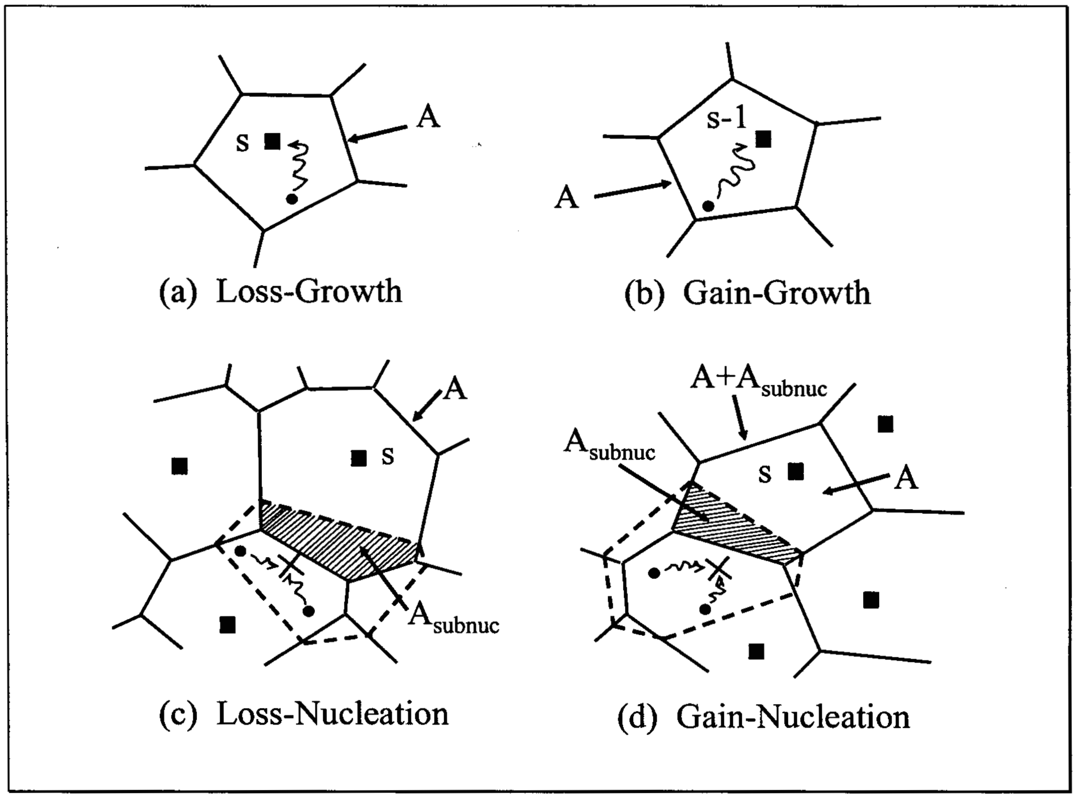

Figure 1. Schematic of loss and gain terms for $N_{s,a}$. For CZ's of area A, (a) loss due to aggregation with an island of size s; (b) gain due to aggregation with an island of size s-1. For islands of size s, (c) loss due to nucleation (×) with probability $P_{s,A}$ overlapping a CZ of area A; (d) gain due to nucleation (×) with probability $P^{+}_{s,A}$ overlapping a CZ of area $A+A_{subnuc}$. CZ boundaries of pre-existing (just-nucleated) islands are indicated by solid (dashed) lines.

Next, we apply $\Sigma_A A\bullet$ to (3). Accounting for the properties of nucleation terms [12], one obtains

$$d/dt\,(A_s N_s) = -F\,(A_s)^2 N_s + F\,(A_{s-1})^2 N_{s-1} - A_{subnuc}(s)\,P_s\,d/dt\,N_{av} - \varepsilon_s + \varepsilon_{s-1} \qquad (5)$$

where $A_{subnuc}(s)\,P_s = \Sigma_A A_{subnuc}(s,A)\,P_{s,A}$, and $\Sigma_s A_{subnuc}(s)\,P_s = A_{avsubnuc}\,M_0$. (6)

Here, $A_{avsubnuc}$ denotes the average area of the individual portions or *subsets* of the CZ's of just-nucleated islands overlapping each existing CZ. The "correction" terms $\varepsilon_s = F\,\Sigma_A (A-A_s)^2 N_{s,A}$ give a measure of the significant variance of the CZ area distribution for islands of size s.

REALISTIC CHARACTERIZATION OF THE NUCLEATION PROCESS

The JPD evolution equation involves *two key quantities* characterizing nucleation: $P_{s,A}$ and $A_{subnuc}(s,A)$. For these quantities, we assume the natural scaling forms [12]

$$P_{s,A} \approx (N_{s,A}/N_{av})\,q(\alpha),\ A_{subnuc}(s,A) \approx A_{av}\,a_{subnuc}(\alpha),\ \text{and set } A_{avsubnuc}=A_{av}\,a_{avsubnuc}\,, \qquad (7)$$

arguing that q and a_{subnuc} should depend primarily on CZ area rather than on island size s.

The behavior of a_{subnuc} follows from geometric considerations. Nucleation occurs primarily near the boundaries of existing CZ's , the CZ of the just-nucleated island overlapping on average $M_0 \approx 5\text{-}6$ existing CZ areas. Thus, the extent of overlap should be *proportional* to the areas of the individual CZ's, so that $a_{subnuc}(\alpha) \approx \mu\cdot\alpha$, where likely $\mu \approx a_{avsubnuc}$. To estimate μ, note that $A_{avnuc} = A_{avsubnuc}\,M_0$ gives the average (total) area of the CZ's of just-nucleated islands, and set $A_{avnuc} = A_{av}\,a_{avnuc}$. Previous studies for point islands showed that $a_{avnuc} \approx 0.97$ [5,9], so that $\mu \approx a_{avsubnuc}=a_{avnuc}/M_0 \approx 0.18$. Indeed, simulation data for point islands confirms that $\mu \approx 0.16$ [12].

Next, we write $q(\alpha) \sim \alpha^{neff}$. Note that the probability for nucleation to occur within a circular CZ of area A, with an island in the center, scales roughly like A^3, suggesting $n_{eff} \approx 3$. Clearly, this analysis is too simplistic. The exact $P_{s,A}$ incorporates contributions from nucleation events occurring not only within the cell of area A, but also in neighboring cells. Perhaps more significantly, the CZ and island geometry generally do not have circular symmetry. Simulation results for point islands for $q(\alpha)$ versus α may be fit by a form, $q(\alpha) \approx c\cdot\alpha^{neff}$, where $n_{eff} \approx 2$ for small α, decreasing to $n_{eff} \approx 1.2$ for $\alpha \approx 1.5$ [12]. Thus, we use $n_{eff} \approx (4+\alpha)/(2+\alpha)$.

ANALYSIS OF THE SCALED EVOLUTION EQUATIONS

Rather than analyze the scaled form of the evolution equation (3) for the full JPD, we instead focus on analysis of the reduced equations (4) and (5). We shall exploit the result that $s_{av} \sim \theta^z$, with z=2/3 for point islands. Analysis of (4) yields the *fundamental equation for f(x)* [7]:

$$(1\text{-}2z)f(x) - zx\,d/dx\,f(x) = -\,d/dx[a(x)f(x)],\ \text{so } f(x)=f(0)\exp[\textstyle\int_0^x dy\{(2z-1)-a'(y)\}/\{a(y)-z\cdot y\}]. \qquad (8)$$

The latter provides an *exact* relation for f(x) in terms of a(x) and z [7]. Analysis of (5) requires adoption of the scaling forms (7) for the key quantities characterizing nucleation. Then, one obtains the *fundamental equation for a(x)* [12]:

$$[a(x)-z\cdot x]\,d/dx\, a(x) = (1-z)[a(x) - \int d\alpha\, a_{subnuc}(\alpha)q(\alpha)G(\alpha-a(x))] - v\,[d/dx\, f(x)]/f(x). \qquad (9)$$

Upon eliminating f(x) from the last term of (9) using (8), one obtains [12]:

$$d/dx\, a(x) = \frac{(1-z)[a(x) - \int d\alpha\, a_{subnuc}(\alpha)q(\alpha)G(\alpha-a(x))][a(x)-z\cdot x] - (2z-1)\,v}{[a(x)-z\cdot x]^2 - v}, \qquad (10)$$

In (10), we input $a_{subnuc}(\alpha)=\mu\cdot\alpha$, $q(\alpha)=c\cdot\alpha^{neff}$, with suitable n_{eff}, and Gaussian G. This leaves $v\approx0.08$ (from simulations), and $\lambda=\mu\cdot c$, which is chosen to satisfy normalization conditions.

We now discuss two consequences of (10). *First*, for point islands, $a(x)-z\cdot x$ decreases from ≈0.92 for x=0, to *below* $v^{1/2}\approx0.28$ for large x. Thus, the numerator and denominator of (10) must *simultaneously* vanish at some $x=x_s$ where $a_s=a(x_s)=z\cdot x_s+v^{1/2}$. *Second,* what is the asymptotic form of a(x) versus x, for large x? Simulations for point islands suggest that a(x) becomes close to z·x, for large x. Equation (10) predicts that if $a(x)-z\cdot x\to0$, *then* one has that $d/dx\, a(x) \to 2z-1$. Thus, the apparent singularity of f(x) in (8), when the denominator of the integrand, a(y)-z·y, vanishes, would be removed by simultaneous vanishing of the numerator.

We now examine the predictions of the rate equations for a(x) with a(0)=0.9. Ideally, one would use (10) to determine a(x), but the singular behavior noted above creates complications [12]. Thus, to obtain an initial check on our theory while avoiding these complications, we use (9) where the last term on the RHS is determined from simulation data for f(x). Fig.2b shows that the result of integrating this equation recovers all the key features of a(x) apparent in the simulation data of Fig.2a. These include both a plateau for x<1, followed by a rapid increase for x>1. However, the result of integrating (9) neglecting the last term, i.e., effectively setting the variance v to zero, shows much poorer agreement with the simulation data. Taken together, these results support the validity of our evolution equations for a(x). They further demonstrate the importance of suitably describing nucleation through $q(\alpha)$, and of incorporating "correction" terms in (9) or (10) associated with the significant spread in CZ areas for each island size.

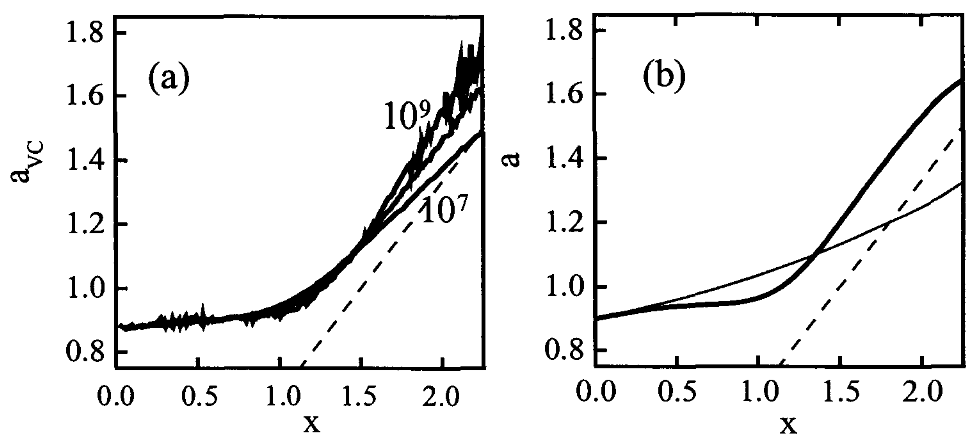

Figure 2. (a) Exact a(x) versus x from VC's for point islands at 0.1ML with $h/F=10^7$-10^9; (b) Numerical solution of (9) for a(x) versus x, with $c\mu=0.675$ (thick curve). The result of ignoring the last term on the RHS of (9) is also shown (thin curve). The dashed lines show $a=(z=2/3)\cdot x$.

DISCUSSION AND FUTURE DIRECTIONS

A primary contribution of our treatment [12] is the development of equations (9) and (10) for a(x) incorporating a realistic treatment of spatial aspects of nucleation, and correct scaling properties of the JPD. These features are missing in previous theories [9,10]. These equations show directly how the details of the nucleation process influence the form of a(x) versus x. This variation is of fundamental significance as it controls the shape of f(x) [7]. Some remaining inadequacies of our theory, including singular behavior of (10), are discussed in [12].

Another potentially more significant consequence of this work is in highlighting spatial or "geometric" aspects of nucleation: for irreversible island formation, most nucleation occurs in the steady-state regime where there is a rough balance between deposition and aggregation of adatoms [12], and most new islands are nucleated nearby CZ boundaries [14]. This suggests a new strategy for simulation of submonolayer deposition [15] wherein both island nucleation and growth are prescribed geometrically, rather than by explicitly simulating terrace diffusion of adatoms or solving the corresponding diffusion equation (which are computationally expensive). Specifically, in the steady-state regime, island growth rates are simply determined by CZ areas, as above, and island nucleation occurs "along" CZ boundaries, where adatom density is highest, but with suitable weighting to reflect variation in this density. (In the initial transient regime, where adatom density is still building up, island nucleation occurs randomly, although not in the vicinity of existing islands, and island growth is not significant.) We have tested this approach, and find that it is very successful in recovering the correct island size distribution [15].

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REFERENCES

1. J.A. Venables, *Philosophical Magazine* **27**, 693 (1973).
2. S. Stoyanov and D. Kashchiev, *Current Topics in Materials Science* **7**, 69 (1981).
3. J.G. Amar and F. Family, *Phys. Rev. Lett.* **74**, 2066 (1995).
4. P.A. Mulheran and J.A. Blackman, *Phys. Rev.* B **53**, 10261 (1996).
5. M.C. Bartelt and J.W. Evans, *Phys. Rev.* B **46**, 12675 (1992); *Surf. Sci.* **298**, 421 (1993).
6. G.S. Bales and D.C. Chrzan, *Phys. Rev.* B **50**, 6057 (1994).
7. M.C. Bartelt and J.W. Evans, *Phys. Rev.* B **54**, R17359 (1996).
8. J.A. Venables and D.J. Ball, *Proc. Roy. Soc. London*, Ser. A **322**, 331 (1971).
9. P.A. Mulheran and D.A. Robbie, *Europhys. Lett.* **49**, 617 (2000).
10. J.G. Amar, M.N. Popescu, and F. Family, *Phys. Rev. Lett.* **86**, 3092 (2001).
11. J.W. Evans and M.C. Bartelt, in "Morphological Organization in Epitaxial Growth and Removal" (World Scientific, Singapore, 1998), p.50; *Phys. Rev.* B **63**, 235408 (2001).
12. J.W. Evans and M.C. Bartelt, *Phys. Rev.* B **66**, 2354xx (2002).
13. M.C. Bartelt, A.K. Schmid, J.W. Evans, & R.Q. Hwang, *Phys. Rev. Lett.* **81**, 1901 (1998).
14. J.W. Evans, J.B. Hannon, M.C. Bartelt, & G.L. Kellogg, *Bull. Am. Phys. Soc.* **45**, 363 (2000).
15. Maozhi Li, M.C. Bartelt, and J.W. Evans, *Fall 2002 MRS Abstract* **W2.11** (to be published).